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Conservation of $^{87}Sr/^{86}Sr$ isotopic ratios during the winemaking processes of 'Red' wines to validate their use as geographic tracer

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Abstract

$^{87}Sr/^{86}Sr$ has been determined in wines, musts grape juces, soils and rocks from six selected vineyards of 'Cesanese' wine area. Cesanese is a monocultivar wine from a small region characterised by different geologic substrata, a key locality to test the influence of both substratum and winemaking procedure on the $^{87}Sr/^{86}Sr$ of wines. Experimental work has been performed on wines from different vintage years to check possible seasonal variations. The data reveals that $^{87}Sr/^{86}Sr$ does not change through time to validate the selection of wineries performed, and in addition no isotopic variation are observed during winemaking processes. Indeed, no significant isotopic variations have been observed in musts and wines. These findings reinforce the hypothesis that the isotopic signature of wines is strongly related to the bioavailable fraction of the soil rather than to its bulk. The data corroborate the passibility that Sr-isotopes of high-quality wines can be used as a reliable tool for fingerprinting wine geographic provenance. (156 words)

Keywords: Sr isotopes, wines, wine making processes, Cesanese wine.

Highlights

- Sr isotopes are a robust fingerprint to trace the geographic authenticity of wine
- Sr isotopes are not contaminated during the winemaking processes

- Wine has constant $^{87}Sr/^{86}Sr$ composition independent by vintange years
- $^{87}Sr/^{86}Sr$ of the bioavailable soil solutions are related to geologic substratum
- The bioavailable soil solution fraction transfers its isotopic signature to wine

Running title

$^{87}Sr/^{86}Sr$ and the winemaking processes of Red wines

1. Introduction

Long lived isotope ratios of heavy elements of geological interest, such as $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, have in the last decades gained importance in tackling the issue of geographical food traceability as well as in solving issues related with archaeological, environmental, medical and forensic sciences (Hoogewerff et al., 2001; Podio et al., 2013; Vorkelius et al., 2010). This increasing consideration is mainly based on the fact that radiogenic isotopic ratios are extensively used either for tracking geological and environmental processes or in dating cosmological and Earth's materials (Capo et al., 1998; Horn et al., 1993; Tommasini et al., 2000). In addition, radiogenic isotope ratios are fractionated neither by low-temperature nor by biogenic processes, then their abundance in geological materials (i.e. minerals and rocks) depends upon: i) the initial radiogenic isotopic abundance, ii) on the age of the rock/mineral, and iii) on their parent/daughter isotope ratio (Dickin, 2005; Stewart et al., 1998; Stille et al., 2009).

Each geologic substratum of vineyards is liable to have its own Sr isotope composition, which can potentially represent a *fingerprint* to trace the wine production provenance (Boari et al., 2008; Marchionni et al., 2013). The use of $^{87}Sr/^{86}Sr$ in tracking wine regional provenance was among the most pioneering application of isotope geology to other sciences (Almeida & Vasconcelos, 2004; Barbaste et al., 2002; Di Paola-Naranjo et al., 2011; Horn et al., 1993). In most of the cases, however, the analytical uncertainty observed in Sr isotopes analyses of wines from literature is larger than most of the rock/soil isotopic variability, giving strong difficulties in matching data of wines with those from geological substrata of the vineyards. Recently, high-precision analytical method for determining $^{87}Sr/^{86}Sr$ has been provided enabling then the direct comparison between data on wines with those of the geological and pedological substrata (Boari et al., 2008; Durante et al., 2015; Marchionni et al., 2013; Mercurio et al., 2014; Petrini et al., 2015).

Although the use of high precision Sr isotopic measurement, in some case discrepancies have been observed between the $^{87}Sr/^{86}Sr$ ratios in wine with those of geological material of the substrata of the vineyards (Boari et al., 2008; Marchionni et al., 2013). This might be due either to adulteration of the analysed wines or to contamination during vine life, with Sr uptake by its roots, and the winemaking processes, To encompass this issue a detailed study on the distribution of $^{87}Sr/^{86}Sr$ in the complete chain of wine production of a 'DOC'-certified Italian 'Red' wine has been undertaken. This experimental study has the aim to verify the possible occurrence of $^{87}Sr/^{86}Sr$ decoupling between the wine and the geological substratum (i.e., rocks).

We determined $^{87}Sr/^{86}Sr$ in rocks, soil, grape, grape juice (must), and wine on six different farms from the '*Cesanese*' wine region in which we followed and verified the good winemaking practices during the years under consideration. The '*Cesanese*' cultivar is a red Italian grape variety that is grown primarily in the Latium district, Central Italy. The '*Cesanese*' Red wine is produced using 100 % of the homonymous grape and it is regulated and certified through three geographically distinct production areas: the *Cesanese di Affile* DOC (*Denomination of Origin Verified* according to the Italian appellation law for wines), *Cesanese di Olevano Romano* DOC, and *Cesanese del Piglio* DOCG (*Denomination of Origin Verified and Guaranteed*, where in addition to geographic provenance also sensorial characteristic of wines are guaranteed). The selected wineries cover the three distinct DOC areas and they are from a geologically well-defined region (Critelli et al., 2007; Giordano et al., 2010), from which a wide isotopic set of data for volcanic rocks is available (Boari et al., 2009a,b; Conticelli et al., 2010).

The final aim of this study is establish direct and unambiguos relationships between Sr-isotope of wines and those of the substrata of their vineyards and to verify that neither the root nor the winemaking processes are able to change them through fractionation and contamination with additives, respectively.

2. Material and Methods

The samples of the oenological chain used for this study (e.g., rocks, soil, grape, grape juice, must, and wine) are from six different wine producers of the three '*Cesanese*' wine areas. The selected wines are indeed from: i) '*Cesanese di Olevano Romano*' consortium (i.e.

Silene, *Colle Canino*, and *Attis* Red wines); ii) '*Cesanese di Affile*' consortium (i.e., *Cesanese di Affile* Red Wine), and from the '*Cesanese del Piglio*' Consortium (i.e. *Romanico* Red wine).

The wines analysed in this experimental study are from small vineyards (some 1-4 ha), owned by high-quality farmers who ensured the grapes provenance and the controlled winemaking procedure. According to the consortia regulation all wines analysed are made by the *Cesanese* red grape variety (monocultivar); this ensure from possible differential elemental uptake from soil *via* the vine roots as seen to occur for REE (Censi et al., 2014).

Multiple wine and must samples have been collected directly from tanks before bottling. Previous studies have shown that $^{87}Sr/^{86}Sr$ in wines from different vintage years is preserved unless contamination occurred (Boari et al., 2008; Durante et al., 2015; Marchionni et al., 2013; Mercurio et al., 2014; Petrini et al., 2015). In this experimental work, however, we decided to use for each winery 5-7 samples of wine and must from a multiple vintage years population to check the conservation of the amount of radiogenic Sr for wines from the same vineyard through the years then to reinforce the significance of the data used for evaluating the winemaking process. Then grape juces have been also sampled to check for the absence of external imputs during the winemaking processes and the oenological chain from raw agricultural fruit to bottled wine.

In addition to wine, must, and grape, volcanic and sedimentary bedrocks along with soils from the vineyards of grape production have been sampled to verify the $^{87}Sr/^{86}Sr$ of the geological substrata of the Cesanese area in comparison with the available data for similar rocks (Conticelli et al., 2010, 2015; Boari et al., 2009a,b). In addition the $^{87}Sr/^{86}Sr$ from rocks and soil of the vineyards substrata are necessary to assess the existing relationships with the Sr isotope composition of wines.

In some cases soils were sampled at different depth to evaluate isotopic variability of the different levels. In addition whole soil and volcanic samples and extracted leached solutions from them have been analysed. This has been done to assess the different Sr isotope composition between the soil and the soil solution that regulates bioavailability for bio-vegetative processes. Considering rock-forming minerals experiencing weathering processes, a differential leaching is to be expected, and only by chance the soil solution will have the same inorganic trace element and isotopic budget of the bulk source rock or soil.

2.1. Sample preparation, digestion and Sr-purification

Rock samples have been brought first to sand-size material (< 2 mm) using a jaw crusher then mechanically split to obtain a representative sample and eventually pulverised to powder-size, grain-size smaller than 100 μ (<400 mesh), using a ball mill. Agate ball mill is used in place of any other pulverisation metal device to avoid possible trace element contamination (Takamasa & Nakai, 2009). Soil samples before splitting and pulverisation have been dried at 60 °C. Grape samples have been washed several times with highly purified Milli-Q® water (18.2 MΩ cm^{-1}) before digestion. Grape musts and wines did not undergo any treatment before digestion.

Successively rock and soil as well as grape, grape must and wine samples have been treated and prepared for mass spectrometer analyses in a clean chemistry laboratory equipped with conditioned (ca. 20°C) and overpressured air ('Class 1000' environment).

Rock, grape, grape must, and wine samples underwent different digestion procedures.

Some 50 mg of of bulk soil and rock samples were digested in cleaned PFA beakers using a 1:4 mixture of concentrated HNO_3 and HF. After 1-2 days at 140°C, solutions were evaporated to dryness, nitrated twice, dissolved in 6N HCl at 120°C, and eventually evaporated to dryness and dissolved again in 1 ml 3N HNO_3. Digestion was performed using clean PFA beakers within horizontal HEPA filtered laminar flow work-stations sited themselves inside a fume cupboard. This environment ensures a low-blank working area. High purity chemical reagents and water during sample treatment has been also used. Concentrated HNO_3 (65-69 wt.%), and H_2O_2 (30 wt.%) were of ultra-pure quality; concentrated HF (40-49 wt.%) was of supra-pure quality; concentrated HCl (37 wt.%) of pro-analysis quality was distilled using a quartz sub-boiling distillation device. Water was treated with two steps of purification to obtain high resistivity Milli-Q® water (18.2 MΩ cm^{-1}). Sr-purification was performed using cation exchange chromatography within a vertical HEPA-filtered laminar flow hood ('Class 100' environment) and high-purity chemical reagents.

In order to emulate the composition of the bioavailable soil solution fraction we used *Unibest* resin capsules (Unibest Inc., Bozeman MT). *Unibest* capsules are filled by ion exchange resins able to mimic the action of plant roots during uptaking of bioavailable substances from soil (Skogley & Dobermann, 1996). The use of *Unibest* capsules overcomes

the problem of the purity level of reagents employed in the traditional soil sequential extraction procedure of the bioavailable component of the soil. It has been shown that *Unibest* resin capsules represent an efficient 'universal-bioavailability' system for measuring inorganics in soils of very different origin and composition (Johnson et al., 2005; Jones et al., 2012; Skogley & Dobermann, 1996).

The ion accumulation into the resin capsules is time-dependent (Dobermann et al., 1994). We performed preliminary experiments on the extraction time needed to obtain the correct amount of Sr for isotopic analyses. The according to Skogley & Dobermann (1996a) some 200 g of soil have been mixed with Mill-Q water and let the *Unibest* spherical capsule (2 cm diameter) sink and stay within the obtained mud solution for some 10 days. Then the capsule has been extracted from the mud solution and rinsed with Milli-Q® water to remove soil residue from the surface, and then put in a cleaned PFA beaker with 20 ml 2N HCl, repeated three times, to extract the chemical elements absorbed from the soil solution. Each time the 20 ml 2N HCl solution was evaporated to dryness and eventually was dissolved in 1 ml 3N HNO_3 for Sr purification. Extracted and purified bioavailable Sr fraction was then loaded onto filament for mass-spec measurement.

Some 10-5 ml of wine, grape must, and grape juice, the latter from the squeezing of grape samples were evaporated to dryness at 90°C in cleaned PFA beakers. The residues were dissolved twice in 3 ml of H_2O_2 (30 wt. %) at 40°C for 1 day and subsequently evaporated to dryness at 90°C. The samples were then dissolved twice in 2 ml HNO_3 (67 wt. %) at 150°C for 1 day, evaporated to dryness and dissolved again in 1 ml 3N HNO_3 for Sr purification (see also Boari et al., 2008; Marchionni et al., 2013). Digested samples were subsequently treated for Sr fraction purification with conventional cation exchange chromatography using disposable Sr-Spec resins (100-150 µm, Eichrom®) in 140 µl pure quartz micro-columns with 3N HNO_3 as eluent and Milli-Q® water water to collect Sr. Care was taken in calibration of the Sr-Spec resins in order to avoid presence of Rb and Ba in the eluted Sr enriched fraction to be mounted on the filament, although possible presence of ^{87}Rb in ultratrace is efficiently burn out during step heating before TIMS measurements.

2.2 Sample loading and mass spectrometry analyses

Following cation exchange chromatography, some 100-200 ng of Sr for each sample were dissolved in 1 µl of 2N HNO_3 and loaded on single Re filaments along with 1 µl of $TaCl_5$ (activator) and 1 µl of H_3PO_5 (fractionation suppressor).

Sr isotopes abundance (^{88}Sr, ^{87}Sr, ^{86}Sr, ^{84}Sr) have been measured in dynamic mode using a Thermo Finnigan™ Triton-Ti magnetic sector field thermal ionisation mass-spectrometer (TIMS) equipped with nine moveable collectors at the Department of Earth Sciences, University of Firenze. Measurements have been carried our using *multi-dynamic* mass collection procedure (i.e., peak jumping) to avoid bias due different faraday cup efficiencies (Avanzinelli et al., 2005). An idle time of 3 seconds has been set before the start of the collection after each jump, to eliminate possible memory effect due to the decay of the signal in the faraday cups (Thirlwall, 1991). *Multi-dynamic* mass collection procedure provides two simultaneous but independent measurements of the $^{87}Sr/^{86}Sr$, which once exponential law corrected and geometrically averaged gives a more accurate and precise $^{87}Sr/^{86}Sr$ value (Avanzinelli et al., 2005). The instrumental mass bias has been corrected *off line* with the $^{88}Sr/^{86}Sr$ ratio measured on the *main* configuration using the natural value ($^{88}Sr/^{86}Sr_N$ = 8.375209) and an *exponential fractionation law* (Thirlwall, 1991). ^{85}Rb has been also monitored during Sr measurements on the L2 collector to correct for residual contribution (i.e., isobaric interference), if any, of ^{87}Rb to ^{87}Sr, using the natural $^{87}Rb/^{85}Rb$ (i.e., 0.386). Each single isotope measurement, consisting of 120 cycles, has been performed using a signal of ca. 4 V on mass 88. Procedural blank was <200 pg resulting in negligible sample correction. The external precision of NIST SRM987 international reference sample for period of this study was $^{87}Sr/^{86}Sr$ = 0.710251±10 (2σ, n=20), whilst the long-term long-term mean value was $^{87}Sr/^{86}Sr$ = 0.710248 ± 16 (2σ, n =173, equivalent to an error of 23ppm), identical to the widely accepted recommended value of Thirlwall (1991), $^{87}Sr/^{86}Sr$ = 0.710248 ± 11. The within run precision (i.e., $2\sigma_m$: internal precision) of $^{87}Sr/^{86}Sr$ measurements has been typically ≤10 ppm.

2.3. Statistical analysis

Classical linear regression analysis was used to model the relationship of the $^{87}Sr/^{86}Sr$ isotopic value for musts (*y*) and wines (*x*) thus taking into account that only must (*y*) is the variable subjected to uncertainty. However in our case both values *x* and *y* are subject to errors and the linear Deming regression (Deming, 1943) was also applied for comparison. In

this regression technique the errors on x and y are considered independent and the ratio of their variance known and equal to 1 when the measurement method is the same or, alternatively, different from 1 when the variance of the errors can be estimated.

The one-way analysis of variance (ANOVA) was considered the appropriate tool (Scheffé, 1999) to simultaneously compares the behaviour of a variable ($^{87}Sr/^{86}Sr$ isotopic value) measured on diverse data groups (rocks, musts and wines in our case). The requirements of the method are for independent observations, normally distributed data in each group and equal variances for all groups. Since these are rarely met when working with applied geochemical and environmental data, also the non-parametric version was used (Kruskal–Wallis one-way analysis of variance by ranks, Spurrier, 2003) to avoid mistakes in the interpretation.

3. Results and discussion

The Sr isotope compositions of wine, must, grape juice, and grape from the different vineyards are reported in Table 1a, whilst those of soil, soil leachate, and bedrock are reported in Table 1b. Descriptive statistics of the overall Sr isotopic measurements performed on the different sample populations are reported in table 2, whilst results of the ANOVA test are reported in the electronic supplementary material.

3.1 Evaluation of the samples populations

To ensure the possibility that Sr isotope composition of wine and must used for this experimental study are statistically representative for being considered as a geographic provenance tracer no yearly variability should be observed. Marchionni et al. (2013) have shown that in red bottled wines from different vintage years of the same geological area the Sr-isotope composition is preserved unless possible contamination, although in some cases within area variability has been observed possibly due to mixing with products characterised by different isotopic signatures.

In Figure 1 are shown the $^{87}Sr/^{86}Sr$ values in wines from five different vineyard of the *'Cesanese'* wine region through the vintage years. Each vineyard under consideration has its own geologic substratum, with vineyards of *Romanico*, *Attis* and *Silene* I wines rooted on volcanic rocks of the Colli Albani volcano (Boari et al., 2009a), and vineyards of *Silene II* and *Colline di Affile* wines rooted on sedimentary rocks. With exception of *Silene* wines the

Romanico, *Attis*, and *Colline di Affile* wines show constant and reproducible Sr-isotope compositions independently of the wine vintage year (Fig. 1; see 3.2 for the rationale to consider wine along with grape must and grape for statistical calculation). The *Romanico* wines from the 2008, 2009, 2010, and 2011 vintages has, indeed, an average $^{87}Sr/^{86}Sr$ = 0.709982 (RSD 0.043%). The *Attis* wine from the 2006, 2007, and 2010 vintages has an average $^{87}Sr/^{86}Sr$ = 0.709705 (RSD 0.164%). Incidentally, the wine from the 2010 vintage has the highest $^{87}Sr/^{86}Sr$ and different from the grape of the same vintage, which is similar to the other *Attis* samples (Table 1). This discrepancy is readily explained because the producers during the 2010 winemaking processes added also grapes from another vineyard located to the south-east of Olevano Romano with geologic substratum consisting of Late Miocene sandstones with a highly radiogenic Sr isotope signature (Table 1b). Neglecting the 2010 wine sample, the *Attis* wines has an average $^{87}Sr/^{86}Sr$ = 0.709924 (RSD 0.004%). The *Cesanese di Affile* wines from the 2005, 2009, 2010, and 2011 vintages has an average $^{87}Sr/^{86}Sr$=0.709020 (RSD 0.049%). On the other hand, the *Silene* wine from the San Giovenale (I) and Cereto (II) vineyards (Table 1a) show large isotopic differences in the isotopic signature due to their different substrata (Table 1b). In addition, *Silene* wine from vineyard I (San Giovenale) show an abrupt jump of $^{87}Sr/^{86}Sr$ values from 0.709168±5 (vintage 2003) and 0.709177±5 (vintage 2005) to 0.709629±5 (vintage 2008), 0.709670±6 (vintage 2010), and 0.709595±6 (vintage 2011). Farmer declared that during the 2003 grape growth season lime to the vineyard substratum of the vineyard I (San Giovenale) was added to correct the pH of the soil to the soil. The addition of lime, with a likely $^{87}Sr/^{86}Sr$ value of 0.709 (as the average value of seawater; Palmer & Elderfield, 1985; Edmond, 1992), is reflected in a lower Sr isotope composition of the 2003 vintage, with a protracted action thought the 2005 and 2006 vintages (Table 1a). The increase of the $^{87}Sr/^{86}Sr$, approaching the values of the volcanic substratum (Boari et al., 2009a), in the products since 2006 vintage year indicates that no further addition of limes was performed. The farmer also declared for the *Silene* wine of vineyard II (i.e., Cerreto) only the vintage 2010 was entirely make with grapes from the II vineyard whilst the 2011 was made with mixed grapes from both vineyards, having different geological substrata, thus explaining the drop from 0.710586±8 to 0.709774±5 (Table 1).

In summary, replicate high precision $^{87}Sr/^{86}Sr$ analyses of wines from the same vineyard and produced with harvests from different vintage years show the consistency of Sr-isotope values through time. As a confirmation the discrepancies observed are usually related either to mixing of grapes from different vineyards during the winemaking processes or to addition of lime to the soil of the vineyard for agricultural purpose. Indeed, addition of lime to the vineyard substratum of *Silene* wine in the 2003 explains the lower $^{87}Sr/^{86}Sr$ values of 2003, 2005, and 2006 vintages with respect to values of the 2008, 2009, and 2010 vintages (Fig. 1). The Sr isotope composition of the 2010 vintage *Attis* wine is higher than other *Attis* wines and the 2010 grape (Fig. 1, published as electronic supplementary material) because the producer added grapes from another vineyard located in a sandstone substratum. These preliminary checks helped to better refine the population used for the further steps of this study.

3.2 $^{87}Sr/^{86}Sr$ does not change during winemaking processes

To evaluate the effect of winemaking processes in the production of red wine, grape juice and must have been analysed and compared with the values of $^{87}Sr/^{86}Sr$ of wine samples (Table 1a). Grape juices, musts, and wines from the same vineyard and vintage years display similar $^{87}Sr/^{86}Sr$ values within the calculated standard deviation of each wine (Table 2). Indeed, considering that no variation has been observed in wines (Fig. 1, published as electronic supplementary material), musts and grape juices (Table 1), the obtained data have been then used as a whole calculating statistics for each type of product from the same vineyard. Then in table 2 the statistics of the overall $^{87}Sr/^{86}Sr$ measurements obtained during the experimental work are reported.

Figure 2a reports correlation between wines and musts from the same vineyard with values approaching the 1:1 correlation line, at least within the standard deviation brackets. The largest standard deviations, with mean values falling well outside of the 1:1 correlation line, are shown by the *Silene II* and the *Attis* wines (Tables 1a and 2). The two outlayers observed correspond to the wines that were produced using mixing between grapes from vineyards with different geological substrata. Grape juices has been also analysed but not reported in the graph of figure 2 due to the few data available, but their $^{87}Sr/^{86}Sr$ plot well within the standard deviation of must and wines (tables 1a and 2, the former published as electronic supplementary material).

To obtain a model for the relationship between wines and musts a linear fitting was calculated and reported in Figure 2b. Internal dashed curves are the confidence bands defining the area that has a 95% chance of containing the true regression line. External dashed curves represent the prediction band, which is the area in which 95% of all data points are expected to fall. The regression equation is given by ($^{87}Sr/^{86}Sr$ must) = 0.01257 + 1.0177 ($^{87}Sr/^{86}Sr$ wine) with R^2 equal to 0.94 and slope values statistically significant ($p < 0.01$). Deming regression (Deming, 1943), applied when both values *x* and *y* are subject to uncertainty as in our case, leads to the model ($^{87}Sr/^{86}Sr$ must) = -0.04915 + 1.0693($^{87}Sr/^{86}Sr$ wine). If the $^{87}Sr/^{86}Sr$ isotopic value is considered a dependent variable measured on different groups of data as rock, must and wine the one-way analysis of variance (ANOVA) is appropriate to test for existing differences. Results are reported in the electronic supplementary material. These indicate that the data grouping is not statistically significant for the $^{87}Sr/^{86}Sr$ isotopic value, thus the correlations observed are statistically consistent. Similar results were obtained for the non-parametric version of ANOVA (Kruskal–Wallis one-way analysis of variance by ranks; Spurrier, 2003).

In summary, Sr isotopes are preserved during the winemaking processes of good manifacture practices for $^{87}Sr/^{86}Sr$ determination, performed at the precision levels of geological materials (Thirlwall, 1991), on high quality wines and related grape juices.

3.3 Matches between $^{87}Sr/^{86}Sr$ of oenological food chain and those of the substratum

The vineyards from flatlands of the Cesanese consortia are characterised by volcanic rocks in their geological substratum, dominated by pyroclastic rocks erupted by the Colli Albani volcano (e.g., Boari et al., 2009a; Giordano et al., 2010). On the other hands, vineyards from hills are characterised by substrata made up by Mesozoic to Tertiary sedimentary rocks (limestone, marlstone, sandstone; Critelli et al., 2007). $^{87}Sr/^{86}Sr$ determined on rocks and soils sampled from substrata of the vineyards of production of the wines considered in this study are well within the ranges of measured $^{87}Sr/^{86}Sr$ for volcanic and sedimentary rocks of the Cesanese area and of the Italian peninsula in general (Boari et al., 2009a; 2009b Conticelli et al., 2015).

Marchionni et al. (2013) has shown that at a very large scale $^{87}Sr/^{86}Sr$ of wines matches the $^{87}Sr/^{86}Sr$ isotopic values of the geological substrata of the areas of productions, especially when the rocks of the substrata are of volcanic origin. This suggests that $^{87}Sr/^{86}Sr$

may represent a robust tool in tracing geographic provenance of wines. However, Marchionni et al. (2013) have also shown that in some cases $^{87}Sr/^{86}Sr$ variability in wines is larger than expected from the analyses of the geological substratum (i.e., rocks). In the present study to exploit the origin of radiogenic Sr, and to evaluate their influence we sampled in detail and analysed the rocks making the geological substratum of each vineyard (Table 1b, published as electronic supplementary material). Figure 3 reports the $^{87}Sr/^{86}Sr$ together with the 1:1 correlation line. If exception is made for the *Cesanese di Affile* wine from *Colle Faggiano* vineyard, which plots along the 1:1 line, the other wine/rock pairs plot at higher $^{87}Sr/^{86}Sr$ with respect to 1:1 line indicating that wines are less enriched in radiogenic Sr with respect to the rocks of the substrata of their vineyards (Fig. 3). This feature is mainly observed in wines from vineyards settled over sedimentary bedrocks rather than those on volcanic ones. Indeed, wines from vineyards on volcanic rocks plot not too far from the 1:1 line (Fig. 3) and well within the range of the $^{87}Sr/^{86}Sr$ values of the Alban Hills volcano (Boari et al., 2009a; Conticelli et al., 2002).

Halicz et al. (2008) have shown that significant difference between the $^{88}Sr/^{86}Sr$ fractionation in soils could have an effect on the calculated fractionation factor and thus on the corrected value of the $^{87}Sr/^{86}Sr$ ratio of soils, but correction would only affect the values of high-precision measurements. In our cases the discrepancies observed are three order of magnitude larger than those due by $\delta^{88}/^{86}Sr$ fractionation in surficial environments (Halicz et al., 2008). Thus possible causes of the deviation of $^{87}Sr/^{86}Sr$ of wines from vineyards on sedimentary substrata by the expected geological $^{87}Sr/^{86}Sr$ values have been investigated in details by Braschi (2015, pers. Comm.). Here we investigated only the cases in which the deviation is observed in vineyards with geological substratum made of volcanic rocks.

Then for *Romanico* and *Silene Ib* vineyards we have performed $^{87}Sr/^{86}Sr$ in wines, musts, soils at different depths and underlying rocks (Tables 1 and 2, the former published as electronic supplementary material). For soils we performed $^{87}Sr/^{86}Sr$ after leaching experiments to assess the Sr isotope composition of the bioavailable fraction in soil solutions. The data on leached solutions reveal different Sr isotope compositions with respect to the corresponding soil and bedrock (Table 1, published as electronic supplementary material). The Sr isotope composition of wines from vineyards located on volcanic substrata (*Romanico*, *Attis*, and the first *Silene* vineyard) are less radiogenic than the

bulk soil/bedrock but similar to the leached soil solution. Indeed, all of the bioavailable fractions analysed have $^{87}Sr/^{86}Sr$ less radiogenic than the bulk material (Fig. 4), indicating the prevalent contribution to the Sr budget of the soil solution of a 'relatively unradiogenic' phase (e.g. feldspar and glass rather than biotite). In addition, $^{87}Sr/^{86}Sr$ values of leached solutions approach the values of final grape products (must/wine) with decreasing depth finding the possible horizon of roots uptake between 20 and 30 cm depth (Fig. 4).

3.5. Summary and Conclusions

In this study we have shown that, independently from winemaking procedure and vintage year, wine inherits its Sr isotope composition from the vineyard pedogenetic substratum, making $^{87}Sr/^{86}Sr$ a paramount candidate for being a robust and technologically advanced scientific tool for assessing of authenticity of the geographic provenance issues. As a corollary, the observed discrepancies in Attis wines reinforce the results of our study in that we could directly measure the Sr isotope variation in wine forced by external causes (i.e., lime addition and grape mixing).

The selective extraction of chemical elements by vine-roots, according to their bioavailability, limits the precise correspondence between $^{87}Sr/^{86}Sr$ in bulk soils and wines, then further detailed studies are needed to scientifically demonstrate the mechanism for Sr-isotope variability in wines from extremely complex sedimentary substrata. Indeed, the bioavailable organic and inorganic substances in soil solutions differ from the bulk soil composition and can be either extremely variable in clastic and polymineral weathered rocks (soils on sandstones, and granites), or negligible in more homogeneous weathered rocks (soils on marls, clays, limestones, glassy volcanic rocks) as shown in this study.

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Figure Captions

Figure 1 – $^{87}Sr/^{86}Sr$ compositions of wines of the five sampled vineyards of the Cesanese consortia collected from the 2003 through 2011 vintage years.

Figure 2 – a) Relationships between $^{87}Sr/^{86}Sr$ in wines and that in their original musts. Error bars represent the standard deviation of the mean values for the whole isotope analyses performed on the samples. b) Linear regression model for $^{87}Sr/^{86}Sr$ in wines and musts. Internal dashed curves are the confidence bands defining the area that has a 95% chance of containing the true regression line. External dashed curves represent the prediction band, that is the area in which 95% of all data points are expected to fall.

Figure 3 – $^{87}Sr/^{86}Sr$ of wines vs. the Sr-isotope composition in the whole rocks of the substrata of their vineyards. Error bars represents the standard deviation of the mean values for the whole isotope analyses performed on the samples. Grey fields are drawn on the basis of the data from the scientific literature. Data soucers: Conticelli et al. 2015).

Figure 4 – Relationships among $^{87}Sr/^{86}Sr$ in wines and musts and the Sr-isotope values in the substratum (rock and soil). Note that samples are from different depths beneath the vineyards. In addition $^{87}Sr/^{86}Sr$ in soil horizons have been determined on both whole sample and extracted leached solutions, see text for further explanations.

Table Captions

Heading of Table 1 - $^{87}Sr/86Sr$ of a) wines, musts, grapes from Cesanese wine region, b) soils and rocks from the substrata of wineyards of the Cesanese wine region.

Footnote Table 1 - a) $^{87}Sr/^{86}Sr$ values in wine, grape juice, must, and grape from the different vineyards and vintage years of the Cesanese Consortium wine area are reported. All analysed samples are from the Cesanese di Affile red grape variety. b) $^{87}Sr/^{86}Sr$ values in soil, bedrock, and leachable soil solution fraction of the different vineyards of the Cesanese Consortium wine area are reported. Rock type and Lithology columns report the

type of geological substratum of vineyards sampled and analysed, whilst the Sample description column reports the identification name of local geological formations (Giordano et al., 2010). 2 s.e. represent the within run two standard error of the mean referring to the last significant digits. The limestone sample (AF2) from the Colle Faggiano area does not correspond to the substratum of any vineyard; *: leached soil solution fraction using UNIBEST® resins; 2sm: within run two standard error of the mean referring to the last significant digits..

Heading of Table 2 - Descriptive statistics of the samples of the oenological food chain and of their vineyard substrata.

Footnote Table 2 - Dataset used for the statistic definition is formed by the overall Sr-isotopes instrumental measurements.

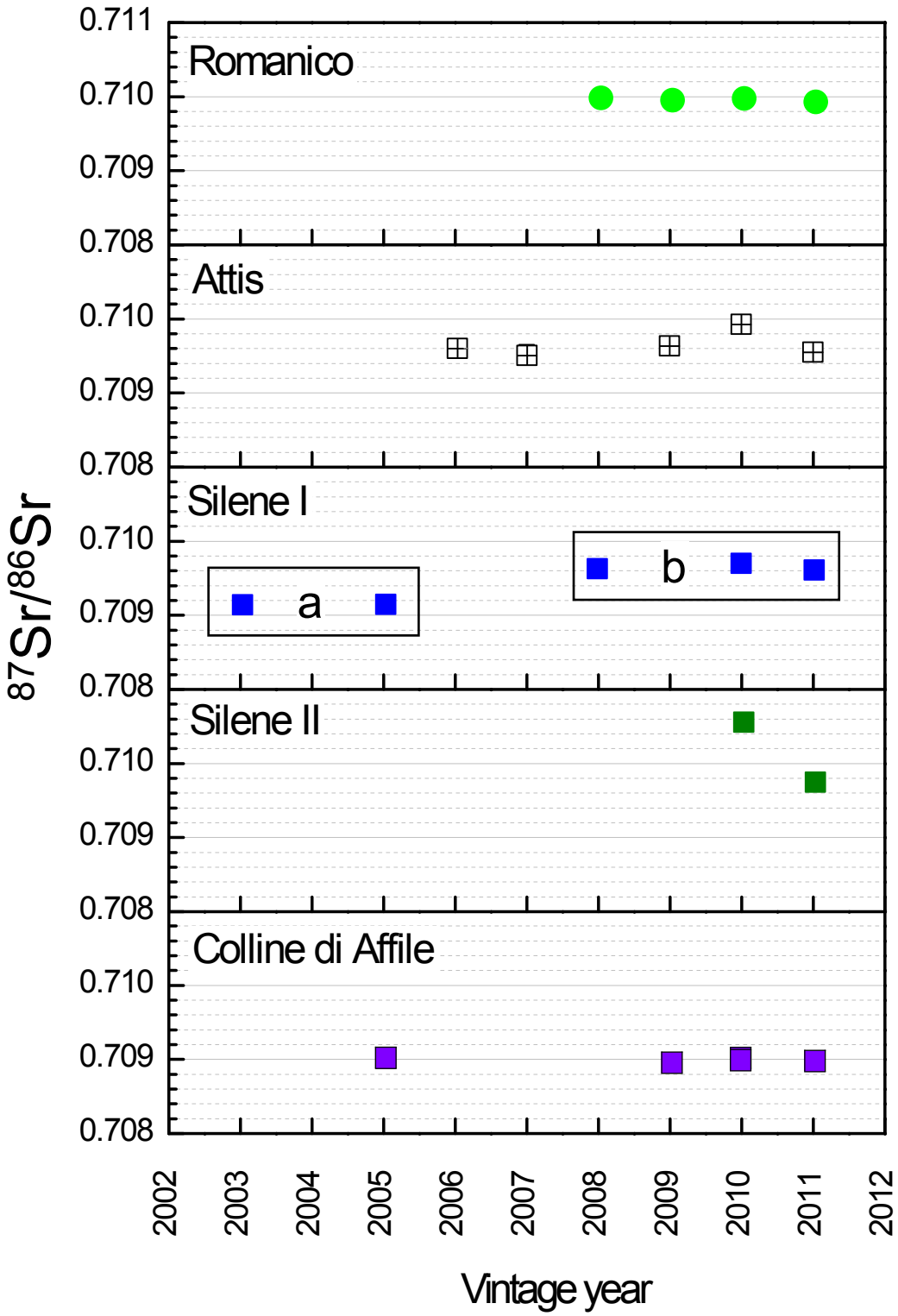

Figure 1 - Marchionni et al. (2014)
Food Chemistry

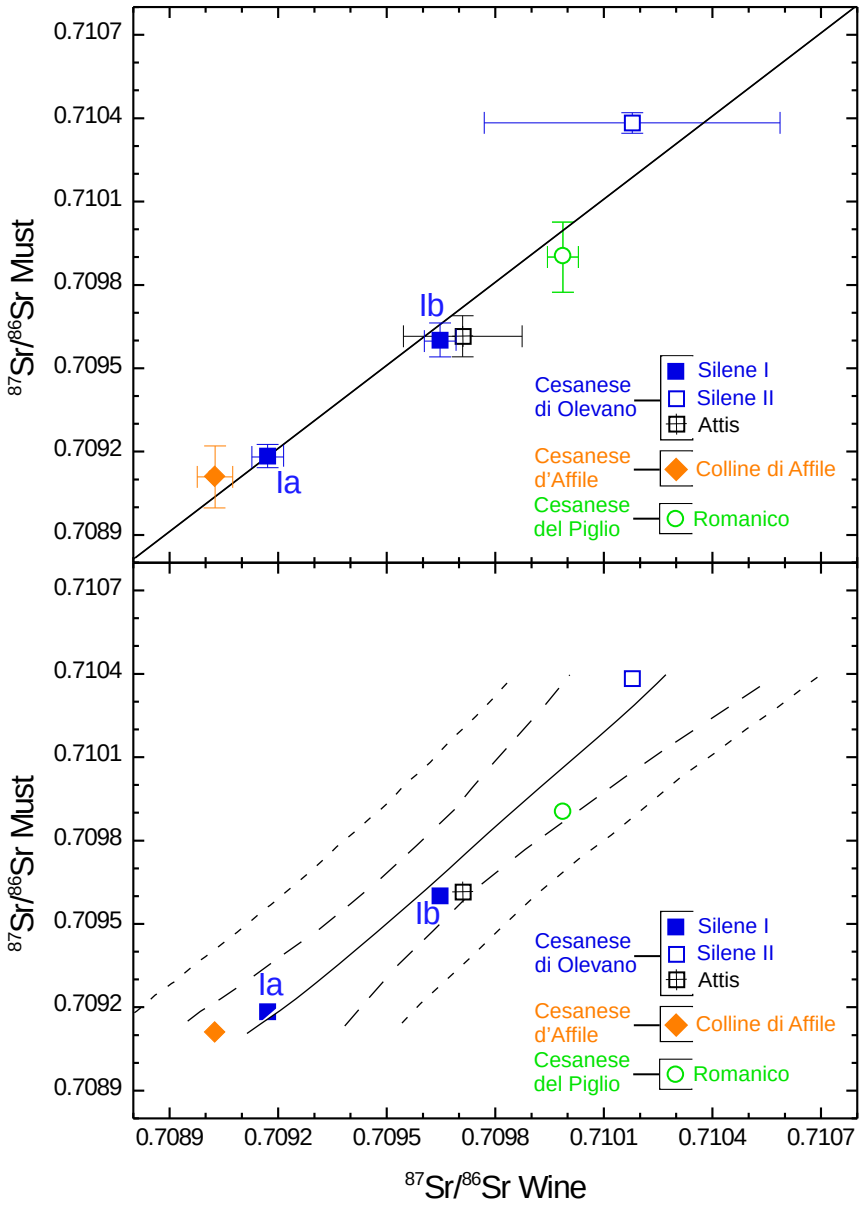

Figure 2 - Marchionni et al. (2014)
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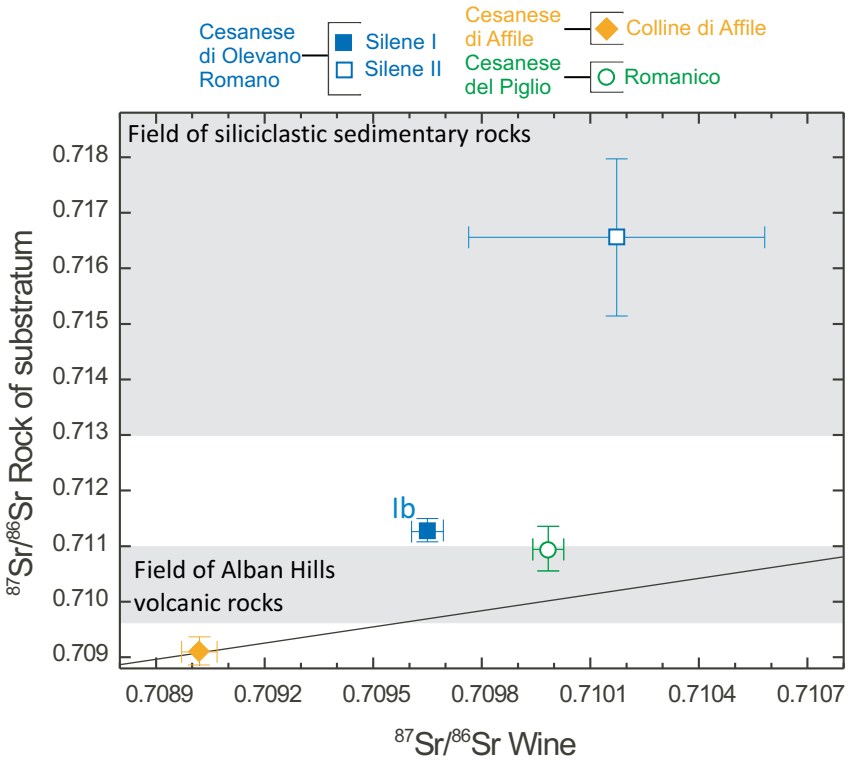
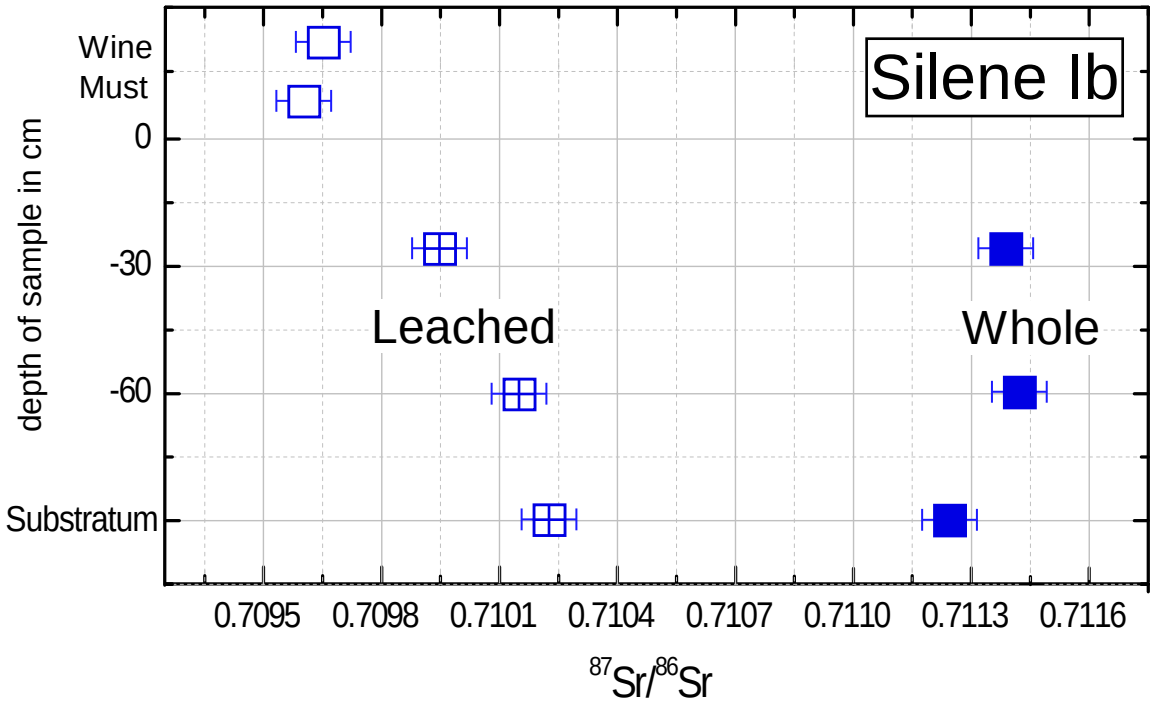


Figure 3 - Marchionni et al. (2014)
Food Chemistry



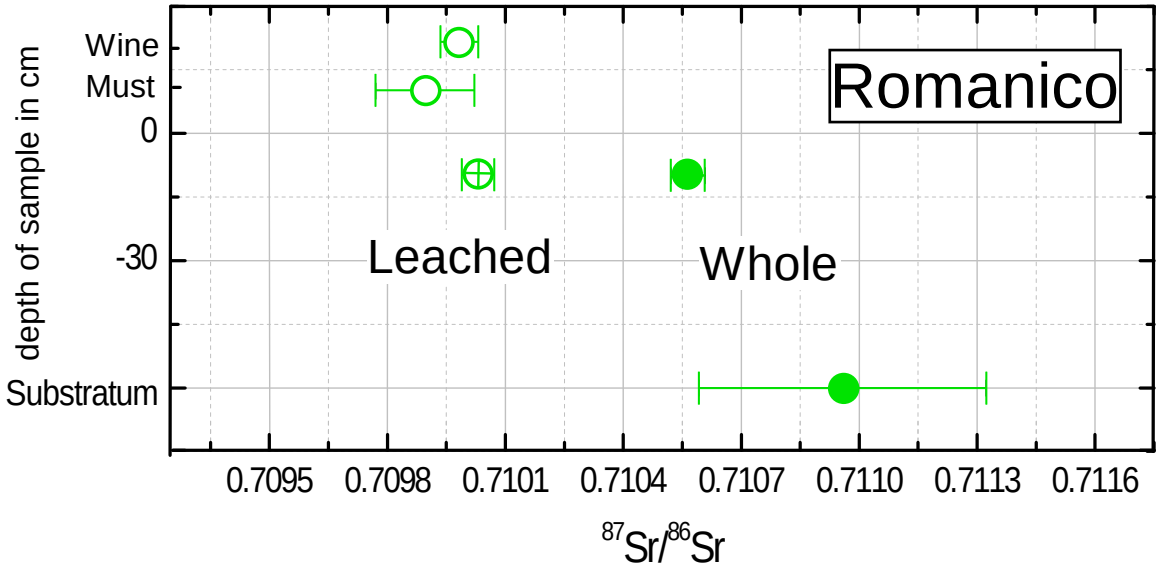


Figure 4 - Marchionni et al. (2014)
Food Chemistry

Table 1a. $^{87}Sr/^{86}Sr$ of wines, musts, grapes from Cesanese wine region.

Wine Production Area	Cultivar	Winery	Vineyard	Wine	Sample	Vintage	$^{87}Sr/^{86}Sr_m$	2 s.e.
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ia	Wine	2003	0.709168	± 0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ia	Must	2005	0.709177	± 0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2006	0.709673	± 0.000007
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Wine	2008	0.709629	± 0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2009	0.709590	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2009	0.709632	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Wine	2010	0.709670	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2010	0.709545	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2011	0.709595	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	Cerreto	Silene II	Wine	2010	0.710586	± 0.000008
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	Cerreto	Silene II	Must	2010	0.710377	± 0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	Cerreto	Silene II	Grape	2010	0.710622	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	Cerreto	Silene II	Wine	2011	0.709774	± 0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2006	0.709633	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2007	0.709548	± 0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Must	2009	0.709512	± 0.000007
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2009	0.709628	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2010	0.709923	± 0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Must	2011	0.709684	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2011	0.709619	± 0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Colle Canino	Colle Canino	Colle Canino	Wine	2010	0.709674	± 0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Colle Canino	Colle Canino	Colle Canino	Wine	2010	0.709771	± 0.000007
Cesanese di Olevano Romano-DOC	Cesanese	Colle Canino	Colle Canino	Colle Canino	Wine	2010	0.709873	± 0.000008
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2005	0.709046	± 0.000006
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2009	0.708978	± 0.000006
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Must	2009	0.709254	± 0.000006
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Must	2009	0.709145	± 0.000006
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2010	0.709025	± 0.000006
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2010	0.709042	± 0.000006
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Must	2010	0.709024	± 0.000005
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Must	2010	0.708991	± 0.000005
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Grape	2010	0.708938	± 0.000007
Cesanese di Affile - DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2011	0.709007	± 0.000006
Cesanese di Affile - DOC	Cesanese	Terre del Cesanese	Colle Passo	Terre del Cesanese	Wine	2010	0.709966	± 0.000005
Cesanese di Affile - DOC	Cesanese	Terre del Cesanese	Colle Passo	Terre del Cesanese	Grape	2010	0.709627	± 0.000007
Cesanese del Piglio - DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Wine	2008	0.709965	± 0.000006
Cesanese del Piglio - DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Wine	2009	0.709989	± 0.000005
Cesanese del Piglio - DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Wine	2010	0.710010	± 0.000006
Cesanese del Piglio - DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Must	2010	0.709782	± 0.000009
Cesanese del Piglio - DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Grape	2010	0.710189	± 0.000024
Cesanese del Piglio - DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Wine	2011	0.709961	± 0.000005
Cesanese del Piglio - DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Must	2011	0.710006	± 0.000005

Table 1b. $^{87}Sr/^{86}Sr$ of soils and rocks from the substrata of wineyards of the Cesanese wine region.

Wine Production Area	Rock type	Lithology	Sample Description	Vineyard	Sample	analysis	$^{87}Sr/^{86}Sr_m$	2 s.e.
Cesanese di Olevano -DOC	Volcanic	Soil	soil on Villa Senni Formation	San Giovenale	- 25 cm	whole	0.711386	± 0.000006
Cesanese di Olevano -DOC	Volcanic	Soil	soil on Villa Senni Formation	San Giovenale	- 25 cm	leached	0.709947	± 0.000005
Cesanese di Olevano -DOC	Volcanic	Soil	soil on Villa Senni Formation	San Giovenale	- 60 cm	whole	0.711421	± 0.000007
Cesanese di Olevano -DOC	Volcanic	Soil	soil on Villa Senni Formation	San Giovenale	- 60 cm	leached	0.710147	± 0.000006
Cesanese di Olevano -DOC	Volcanic	Ignimbrite	Villa Senni Formation	San Giovenale	Rock	whole	0.711238	± 0.000006
Cesanese di Olevano -DOC	Volcanic	Ignimbrite	Villa Senni Formation	San Giovenale	Rock	leached	0.710232	± 0.000006
Cesanese di Olevano -DOC	Sedimentary	Sandstone	Arenaceous-Pelitic Formation	Cereto	Rock	whole	0.717961	± 0.000006
Cesanese di Olevano -DOC	Sedimentary	Sandstone	Arenaceous-Pelitic Formation	Cereto	Rock	whole	0.715146	± 0.000006
Cesanese d'Affile - DOC	Sedimentary	Marlstone	Orbulina Marl	Colle Faggiano	Rock	whole	0.709136	± 0.000006
Cesanese d'Affile - DOC	Sedimentary	Limestone	Briozoan Limestone	Colle Faggiano	Rock	whole	0.708851	± 0.000007
Cesanese del Piglio - DOCG	Volcanic	Soil	soil on Pozzolane Rosse Formation	Colle Cotoverio	- 10 cm	whole	0.710562	± 0.000006
Cesanese del Piglio - DOCG	Volcanic	Soil	soil on Pozzolane Rosse Formation	Colle Cotoverio	- 10 cm	leached	0.710032	± 0.000006
Cesanese del Piglio - DOCG	Volcanic	Ignimbrite	Pozzolane Rosse Formation	Colle Cotoverio	Rock	whole	0.710560	± 0.000006
Cesanese del Piglio - DOCG	Volcanic	Ashfall	Madonna degli Angeli Formation	Colle Cotoverio	Rock	whole	0.711104	± 0.000006
Cesanese del Piglio - DOCG	Volcanic	Surge	Madonna degli Angeli Formation	Colle Cotoverio	Rock	whole	0.711489	± 0.000006
Cesanese del Piglio - DOCG	Sedimentary	Ashfall	Madonna degli Angeli Formation	Colle Cotoverio	Rock	whole	0.711049	± 0.000006
Cesanese del Piglio - DOCG	Sedimentary	Ashfall	Madonna degli Angeli Formation	Colle Cotoverio	Rock	leached	0.710302	± 0.000006
Cesanese del Piglio - DOCG	Volcanic	Ignimbrite	Pozzolane Rosse Formation	Colle Cotoverio	Rock	whole	0.710565	± 0.000006

Table 2. Descriptive statistic of the samples from the oenological food chain and wineyard substrata

Wineyard	Wine	Sample type	Mean	Standard Error	Median	Standard Deviation	Sample Variance	Kurtosis	Sweekness	Range	Min	Max	Counts
San Giovenale		Rock	0.711235	0.000004	0.711235	0.000041	1.71398E-09	0.304635	-0.370324	0.000212	0.711113	0.711325	120
San Giovenale		Rock leached	0.710231	0.000004	0.710231	0.000041	1.71825E-09	-0.485492	0.063509	0.000187	0.710145	0.710332	120
San Giovenale		Soil	0.711405	0.000003	0.711407	0.000048	2.29486E-09	-0.189918	0.228658	0.000231	0.711299	0.711530	240
San Giovenale		Soil leached	0.710049	0.000007	0.710047	0.000109	1.18093E-08	-1.538286	-0.027509	0.000413	0.709819	0.710233	240
San Giovenale	Silene Ib	Must	0.709608	0.000002	0.709608	0.000059	3.5309E-09	-0.234614	-0.031147	0.000329	0.709443	0.709772	600
San Giovenale	Silene Ib	Wine	0.709650	0.000003	0.709652	0.000044	1.90076E-09	0.009289	-0.020265	0.000247	0.709528	0.709775	240
San Giovenale	Silene Ia	Must	0.709182	0.000003	0.709183	0.000038	1.44137E-09	-0.074063	-0.141362	0.000195	0.709070	0.709266	120
San Giovenale	Silene Ia	Wine	0.709171	0.000004	0.709167	0.000040	1.61556E-09	0.224525	0.202043	0.000220	0.709062	0.709283	120
Cerreto		Rock	0.716557	0.000091	0.716544	0.001414	1.99845E-06	-2.013217	0.000335	0.003022	0.715045	0.718066	240
Cerreto	Silene II	Must	0.710379	0.000003	0.710378	0.000037	1.39237E-09	-0.162798	0.045294	0.000190	0.710287	0.710477	120
Cerreto	Silene II	Wine	0.710173	0.000026	0.709930	0.000409	1.67205E-07	-1.927388	0.076921	0.001152	0.709682	0.710834	240
La Selva	Attis	Must	0.709611	0.000003	0.709621	0.000074	5.48651E-09	-0.165869	-0.387209	0.000416	0.709391	0.709806	240
La Selva	Attis	Wine	0.709705	0.000009	0.709640	0.000164	2.69942E-08	-1.367571	0.502110	0.000555	0.709473	0.710029	600
Colle Canino	Colle Canino	Wine	0.709773	0.000014	0.709771	0.000272	7.39412E-08	78.563286	-5.525301	0.004537	0.706286	0.710823	355
Colle Faggiano		Rock	0.708995	0.000010	0.708997	0.000149	2.21643E-08	-1.645372	-0.010544	0.000531	0.708748	0.709279	240
Colle Faggiano	Cesanese di Affile	Grape	0.708950	0.000004	0.708949	0.000047	2.16312E-09	0.249664	0.327964	0.000242	0.708848	0.709090	120
Colle Faggiano	Cesanese di Affile	Must	0.709105	0.000005	0.709088	0.000112	1.24462E-08	-1.148793	0.286425	0.000459	0.708903	0.709362	480
Colle Faggiano	Cesanese di Affile	Wine	0.709020	0.000002	0.709020	0.000049	2.40819E-09	0.022683	-0.069918	0.000341	0.708847	0.709188	600
Colle Passo	Terre del Cesanese	Grape	0.709627	0.000005	0.709625	0.000053	2.77799E-09	0.251209	-0.071310	0.000262	0.709493	0.709755	120
Colle Passo	Terre del Cesanese	Wine	0.709965	0.000003	0.709965	0.000036	1.32506E-09	0.040734	-0.049852	0.000199	0.709861	0.710061	120
Colle Cotoverio		Rock	0.710957	0.000015	0.711048	0.000365	1.33555E-07	-1.220042	0.144197	0.002033	0.709878	0.711911	600
Colle Cotoverio		Soil	0.710564	0.000004	0.710563	0.000043	1.84353E-09	0.052131	0.199281	0.000231	0.710453	0.710684	120
Colle Cotoverio		Soil leached	0.710030	0.000004	0.710025	0.000040	1.59552E-09	-0.572833	0.011641	0.000180	0.709934	0.710115	120
Colle Cotoverio	Romanico	Grape	0.710175	0.000103	0.710180	0.000959	9.19364E-07	53.137531	-5.238089	0.011807	0.702467	0.714274	87
Colle Cotoverio	Romanico	Must	0.709896	0.000008	0.709931	0.000126	1.59497E-08	-0.494381	-0.464343	0.000638	0.709448	0.710086	240
Colle Cotoverio	Romanico	Wine	0.709982	0.000002	0.709981	0.000043	1.82483E-09	-0.325535	0.081127	0.000233	0.709875	0.710109	480

Dataset used for the statistics definition is maked by the overall Sr-isotopes instrumental measurements.

Table 3. Results of multiple comparisons for ANOVA with three groups of data (rocks, must and wine)

(I) index	(J) index	Mean difference (I-J)	Standard Error	Significance	95% Confidence level	
					lower bound	upper bound
1	2	0.002305	0.000967	0.074	-0.000206	0.004817
	3	0.002256	0.000917	0.065	-0.000126	0.004639
2	1	-0.002305	0.000967	0.074	-0.004817	0.000206
	3	-0.000049	0.000809	0.998	-0.002151	0.002052
3	1	-0.002256	0.000917	0.065	-0.004639	0.000126
	2	0.000049	0.000809	0.998	-0.002052	0.002151